Radiochim. Acta **89**, 815–822 (2001)

On the origin of ^{129}I in rain water near Zürich

By C. Schnabel[1,2,*], J. M. Lopez-Gutierrez[3,†], S. Szidat[2,4], M. Sprenger[5], H. Wernli[5], J. Beer[6] and H.-A. Synal[7]

[1] Institute of Particle Physics, ETH Hönggerberg, CH-8093 Zürich, Switzerland
[2] Dept. für Chemie und Biochemie, Universität Bern, CH-3012 Bern, Switzerland
[3] Dpto. Fisica Atomica, Universidad de Sevilla, E-41012 Sevilla, Spain
[4] ZSR, Universität Hannover, D-30167 Hannover, Germany
[5] Institute for Atmospheric and Climate Science, ETH Hönggerberg, CH-8093 Zürich, Switzerland
[6] EAWAG, Ueberlandstr., CH-8600 Dübendorf, Switzerland
[7] Paul Scherrer Institute c/o ETH Hönggerberg, CH-8093 Zürich, Switzerland

(Received March 8, 2001; accepted in revised form May 15, 2001)

I-129 / *Sellafield / La Hague /* ^{129}I / *Atmospheric transport*

Summary. ^{129}I concentrations in precipitation at Dübendorf/Zürich, Switzerland, have been determined with monthly resolution for almost three years in the mid 1990s. The results confirm that annual mean ^{129}I concentrations in precipitation in central Europe have remained about constant since the late 1980s. Liquid and gaseous emissions from the nuclear fuel reprocessing plants at Sellafield and La Hague are discussed as the only possible sources of ^{129}I in precipitation in central Europe. Based on an upper limit estimate for iodine transferred from the sea to the atmosphere, the gaseous discharges constitute the potentially bigger ^{129}I reservoir for precipitation. Moreover, the time dependence of the annual gaseous ^{129}I releases from Sellafield and La Hague correlates much better with the ^{129}I concentrations in precipitation in central Europe since the late 1980s than does the time dependence of the liquid emissions from these sites. At monthly resolution, the ^{129}I concentrations in the precipitation samples close to Zürich exhibit a large variability. A meteorological transport analysis was carried out for four selected months with particularly low or high observed ^{129}I concentrations. It was found that meteorological transport alone, based upon assimilated wind fields and observed precipitation values, can not directly account for the large month-to-month variability.

1. Introduction

^{129}I is a long-lived ($T_{1/2} = 15.7$ Ma) radionuclide whose abundances in the environment have been elevated by several orders of magnitude by human action. The main sources of the prenuclear ^{129}I inventory are spontaneous fission of uranium in the lithosphere and interaction of cosmic ray particles with xenon in the upper atmosphere. The prenuclear equilibrium ^{129}I/^{127}I ratio in the surface hydrosphere has been determined from measurements of recent prenuclear marine sediments at levels around 1.5×10^{-12} [1]. This prenuclear ratio has been drastically enhanced due to the anthropogenic emissions primarily from nuclear fuel reprocessing plants, which are discussed in detail below. A review of modern ^{129}I/^{127}I ratios in the environment is given by Schmidt *et al*. [2]. Here, only the nearly continuous increase of ^{129}I concentrations in an ice core from the Swiss Alps from 1950 to 1986 is mentioned [3, 4]. A calculated mean ^{129}I/^{127}I ratio for the years 1983 to 1986 for that ice core is as high as 5×10^{-8} assuming an iodine content of 1.75 μg/kg, a mean concentration calculated for precipitation in southern Germany (see below). When these data from a high altitude sampling site are compared to data from Bachhuber and Bunzl [5] for rain in Bavaria/Germany 1988/89 with ^{129}I/^{127}I ratios from 6.2×10^{-7} to 9.6×10^{-7}, a further dramatic increase can be seen. Then, the environmental ^{129}I/^{127}I ratios in central Europe seem to have remained stable in the early 1990s [6, 7]. In spite of the fact that all these ^{129}I abundances far away from the emission sources are not seen as radiologically hazardous to people, a detailed observation of the trends of ^{129}I concentrations in Europe is considered necessary. This necessity has become even more important due to the fact that one of the main sources of ^{129}I releases into the environment in the 1980s – the nuclear fuel reprocessing facility in La Hague – has increased its liquid discharges of ^{129}I into the English Channel drastically after 1988 [8] whereas the liquid releases from Sellafield were increased much less from 1988 to 1996 [9, 10]. Moreover, as shown in detail below, both reprocessing plants continue with their ^{129}I discharges at a very high level.

The equilibrium mass of naturally produced mobile ^{129}I in the compartments atmosphere, biosphere, and hydrosphere was estimated at 260 kg [11]. This reservoir was enlarged by atmospheric nuclear weapons tests. For these releases, ^{129}I masses of 50 kg [12], 80 kg ([13, 14]) or 150 kg ([13, 15]) are published. Eisenbud and Gesell [13] give 1.9 GBq ^{129}I emissions per megaton atmospheric bombs. For the yields of atmospheric bomb tests, the estimates vary from 276 megatons [14] to 547 megatons [15]. The Chernobyl accident gave only rise to an atmospheric emission of 1.3 kg ^{129}I [16]. In contrast, Hanford (nuclear fuel reprocessing plant in the north-western USA) emitted from 1944 to 1972 around 260 kg ^{129}I into the atmosphere [17] with high peak emissions in the mid 1940s to early 1950s,

*Author for correspondence
(E-mail: schnabel@particle.phys.ethz.ch).
† Present address: Depto. de Fisica Aplicada I. Escuela Universitaria Politecnica, Universidad de Sevilla, Spain.

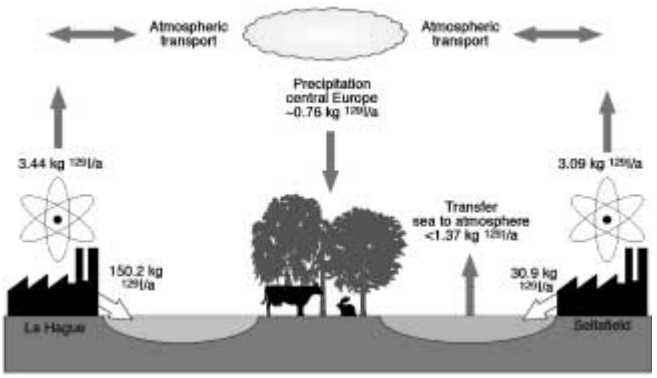

Fig. 1. Schematic illustration of some ^{129}I emission and immission data as annual averages from 1991 to 1996.

when in the early part of that period the gaseous emissions did not pass a filter. The largest additions to the mobile ^{129}I reservoir have been due to the liquid releases of the reprocessing plants at Sellafield (approximately 720 kg from 1961–1997) [8, 10] and at La Hague (approximately 1310 kg from 1966 to 1996) [18]. Compared to these releases the gaseous discharges into the atmosphere of the two sites are relatively small, with approximately 160 kg from Sellafield (1952 to 1999 without 1993) [9, 10] and 58 kg from La Hague (1966 to 1996) [18]. However, it has to be mentioned that the gaseous amount released from Sellafield is only roughly known because of large uncertainties in the emission data for the 1950s [9]. Some important emission and immission data for ^{129}I are shown illustratively in Fig. 1. Although from the sum of all these releases ^{129}I/^{127}I ratios of only approximately 3×10^{-11} would be expected if total mixing of the mobile reservoirs of both isotopes took place, the elevating effect on the iodine isotopic ratio is around 5 to 6 orders of magnitude mainly due to the fact that the deep sea, which constitutes the main mobile ^{127}I reservoir has not yet equilibrated with the anthropogenic ^{129}I emissions [19].

The main goals of the present work are to test the constancy of ^{129}I concentrations in central European rains in the 1990s, and to strengthen the scarce data base of modern ^{129}I concentrations in central Europe. Likely reasons for the large month-to-month variability of the ^{129}I concentrations in precipitation close to Zürich were investigated by applying a detailed meteorological transport analysis.

2. Experimental methods

Any experimental procedure to separate total iodine from a water sample has to ensure that all chemical iodine compounds, *e.g*. iodide, iodate and organic compounds containing iodine, are transformed into a single chemical form, in order to attain isotopic equilibrium between the carrier (^{127}I) and the inherent iodine species in the sample. The method described below equilibrates all iodine species as iodide. It has been tested using ethyl iodide as a model substance for organo-iodine compounds that approximates the chemical behavior of methyl iodide. Methyl iodide is one of the most abundant organic iodine compounds in rain [20]. In these test experiments more than 90% of the iodine present as ethyl iodide were recovered as iodide. The importance of ensuring the destruction of organic iodine compounds has to be emphasized because organic iodine compounds play an important role in coastal rain [21], but also in rain water far away from the coast [22].

The rain was collected over approximately one month periods after addition of at least 3 mg iodide carrier in an alkaline (NaOH), reducing ($NaHSO_3$) solution to avoid any evaporative losses of the carrier. Then, solid NaOH and $NaHSO_3$ were added until pH = 14 and a 0.05 molar bisulfite solution was reached. The strongly alkaline solution is necessary to ensure that possibly present organic iodine compounds are destroyed by hydrolysis whereas the bisulfite results in the reduction of iodate and the iodine originating from the organic compounds, to iodide. In addition, it prevents any evaporative loss of elemental iodine. After shaking the reducing, alkaline water for at least one day (shaking table), the water was acidified with nitric acid to pH = 1 and sodium nitrite was added to oxidize the only iodine species present – iodide – to iodine. Iodide was extracted into chloroform and back-extracted into diluted bisulfite solution after reduction to iodide followed by the precipitation as silver iodide after addition of silver nitrate solution. The isotopic ratio ^{129}I/^{127}I of this material was determined by accelerator mass spectrometry (AMS) using the PSI/ETH facility in Zürich. Details of the AMS measurements are given elsewhere [23]. Typical isotopic ^{129}I/^{127}I ratios of the samples measured after the addition of stable iodine as carrier were 5×10^{-11} to 1×10^{-10}. Chemical processing blanks exhibited ^{129}I/^{127}I ratios of around 2×10^{-13} to 3×10^{-13}.

3. Results and discussion

The radionuclide concentrations of ^{129}I determined in the rain water samples are shown in Table 1.

A large scatter in monthly data is observed. Similar variations have also been measured by Krupp and Aumann for rainfall in Germany [22] and at a shorter time resolution by Lopez-Gutierrez *et al*. for rain in southern Spain [24]. A possible reason for this scatter will be discussed in connection with the application of a meteorological transport model below. The mass-weighted annual mean concentrations of ^{129}I are compared to literature data for central Europe in the 1980s and 1990s in Table 2.

Mass-weighted average relative standard deviations (one sigma) for the annual ^{129}I concentrations at Dübendorf range from 3.7% to 4.3%. Because the original ^{127}I concentration of the rain was not analyzed, an estimate of the inherent ^{129}I/^{127}I ratio of the samples should be based on an assumption of the ^{127}I concentration. The compilation of Fuge and Johnson [25] gives a range from 0.5 to 10 μg/kg I in rain, whereas from the data from Krupp and Aumann [22] an average concentration of 2 μg/kg can be calculated for southern Germany, compared to about 1.5 μg/kg for a site in Bavaria calculated from the data of Bachhuber and Bunzl [5]. Consequently we choose 1.75 μg/kg I as basis to estimate the inherent ^{129}I/^{127}I ratio of the samples analyzed. Moran *et al*. [26] determined 1.7 μg/kg as median iodine concentration of precipitation samples in the US. The mass-weighted means for the inherent ^{129}I/^{127}I ratios are: 3.8×10^{-7} for 1994, 3.2×10^{-7} for 1995 and 4.0×10^{-7} for

Table 1. ^{129}I atom concentrations in water samples from Dübendorf/Zürich, Switzerland.

Date	^{129}I [10^8/ kg]	Date	^{129}I [10^8/ kg]
February 1994	3.60 ± 0.18	June 1995	26.1 ± 1.3
April 1994	17.3 ± 0.87	July 1995	16.3 ± 0.7
May 1994	359 ± 12	August 1995	26.9 ± 1.1
June 1994	37.3 ± 1.3	September 1995	10.1 ± 0.4
July 1994	2.16 ± 0.11	August 1996	5.35 ± 0.3
August 1994	4.97 ± 0.61	September 1996	14.9 ± 0.5
September 1994	127 ± 5	October 1996	52.0 ± 2.0
October 1994	22.9 ± 0.9	November 1996	39.8 ± 0.8
November 1994	2.42 ± 0.11	December 1996	7.45 ± 0.20
December 1994	5.99 ± 0.35	January 1997	70.4 ± 3.0
January 1995	6.94 ± 0.47	February 1997	25.4 ± 2.7
February 1995	29.5 ± 0.1	March 1997	92.8 ± 4.4
March 1995	12.9 ± 0.7	May 1997	445 ± 13
April 1995	103 ± 4	June 1997	22.2 ± 0.4
May 1995	41.5 ± 1.7		

Table 2. ^{129}I atom concentrations in precipitation in central Europe.

Location, year	^{129}I [10^8/ kg]	Reference
Swiss Alps 1983–86	3.30–4.66	[4]
Hannover, Lower Saxony 1986–87	12.1–62.6	[7]
Bavaria 1988	37.5	[5]
Bavaria 1989	76.6	[5]
Dübendorf/Zürich 1994	31.6	[This work]
Dübendorf/Zürich 1995	26.3	[This work]
Dübendorf/Zürich 1996/97	33.1	[This work]
Southern Germany (3 locations) 1995	60.7–88.7	[22]
Lower Saxony open-field inland 1997	20–52	[28]
Lower Saxony open-field inland 1998	33–49	[28]
Lower Saxony open-field inland 1999 (Jan–Jun)	20–30	[28]

1996/97, with relative standard deviations of about 4% for each ratio.

These annual mean isotopic ratios are of the same order of magnitude but slightly lower than those determined by Krupp and Aumann [22] for rain in southern Germany in 1995 (6.9×10^{-7} to 9.7×10^{-7}) and those by Bachhuber and Bunzl [5] for rain in Bavaria in 1988 and 1989 (6.2×10^{-7} to 9.6×10^{-7}). Szidat *et al*. [7] determined mean ^{129}I/^{127}I ratios for open-field rain at different inland locations in northern Germany (1997/98) from 3.6×10^{-7} to 6.6×10^{-7}. The statement by Szidat *et al*. [6, 7] that the ^{129}I/^{127}I ratio has not increased further since the late 1980s thus seems to be confirmed by this work, within the uncertainties of our measurement.

Whereas the inherent isotopic ratios of this work can only be estimated, the annual deposition rates for ^{129}I in mBq m^{-2} a^{-1} can be calculated. In Table 3 the results are compared to the data from Krupp and Aumann [22], Bachhuber and Bunzl [5], and Szidat *et al*. [7], respectively. However, it has to be mentioned that we scaled up the annual deposition rates of this work from the *e.g*. 10 months of sampling to the complete year. Therefore it is very difficult to estimate standard deviations for these data. The decrease in the annual deposition rates for Dübendorf only reflects less precipitation in the months for which samples in 1996/97 were taken compared to 1994/95. This becomes obvious from the comparison of the average annual ^{129}I concentrations in Table 2. For the deposition rates calculated by Wagner [4],

Table 3. Annual deposition rates of ^{129}I in precipitation in mBq m^{-2} a^{-1}.

Location	Year	Deposition rate	Reference
Fiescherhorn, Switzerland	1983–86	0.6–0.9	[4]
Mappenberg, Bavaria	1988	4.0	[5]
Mappenberg, Bavaria	1989	6.6	[5]
Southern Germany	1995	5.8–10.6	[22]
Dübendorf near Zürich	1994	5.34	This work
Dübendorf near Zürich	1995	3.83	This work
Dübendorf near Zürich	1996/97	2.31	This work
Lower Saxony (inland), Germany	1997	1.8–5.7	[28]
Lower Saxony (inland), Germany	1998	3.9–6.6	[28]
Lower Saxony (inland), Germany	1999 (Jan–Jun)	1.9–3.4 (calculated from first 6 months)	[28]

it has to be mentioned that they may be too low due to wind erosion at the high Alpine sampling site and also due to the loss of some organic iodine compounds (see above).

As stated above, the chemical procedure of this work ensures the analysis of all iodine species, whereas for instance a technique using ion exchange without previous destruction of organic iodine compounds will lead to ^{129}I concentrations that are too low. In order to estimate the part of ^{129}I that is present in organic compounds in rain, the sample of November 1996 was divided into two subsamples. One of these subsamples was treated in the way described above whereas the second one was subjected to anion exchange as described by Wagner *et al*. [3]. A first estimate of the part of ^{129}I present in organic compounds in rain water close to Zürich is 15%. Of course more analyses are necessary to confirm this number. Our first result is by far lower than the results obtained by Krupp and Aumann [22] of 37 to 56% organic ^{129}I in rain in southern Germany.

The distribution of liquid ^{129}I discharges from the two major European reprocessing plants has been investigated by Raisbeck *et al*. (*e.g*. [8, 12]). They found ^{129}I from these emissions even in the Kara Sea and proposed ^{129}I as tracer for deep water formation in the North Atlantic [27]. The drastic increase in liquid ^{129}I emissions from La Hague from 1988 to 1995 was observed in Utsira (southern Norway) without delay at a time resolution of one year [8]. Whereas these authors found as early as 1984 ^{129}I/^{127}I ratios up to 10^{-6} in the English Channel they determined isotopic ratios from 3 to 5×10^{-8} as late as 1991 and 1993 in the central North Sea and close to southern Norway [12]. In contrast to these relatively low isotopic ratios, Szidat *et al*. [7, 28] found ^{129}I/^{127}I ratios of about 1.5×10^{-6} in sea water near Cuxhaven (close to the coast of the German Bay) in 1999 and 2000. Because the liquid emissions from La Hague and Sellafield exceeded their direct atmospheric emissions by around a factor of 20 from 1988 to 1995 [9, 10, 18] some authors assumed that the transfer of ^{129}I from the sea into the atmosphere constitutes the dominating source of ^{129}I for the precipitation in central Europe [22]. The other possibility is that the gaseous ^{129}I releases are the most important sources for ^{129}I in central European precipitation. Examples of gaseous ^{129}I emissions dominating ^{129}I in environmental samples are mosses downwind the Sellafield plant analyzed by Rucklidge *et al*. [29]. Later, Moran *et al*. stated that ^{129}I in some environmental samples in the United States was the result of the gaseous discharges from Sellafield and La Hague [26]. In the same paper these authors estimated the global mass of ^{129}I transferred annually from the sea into the atmosphere at only 20 g. Moran *et al*. also proved atmospheric emissions of the Savannah River plant as the ^{129}I source for some environmental samples in the Southeast of the United States [30].

The amount of iodine that is transferred annually from the sea to the atmosphere is not known exactly. Reifenhäuser and Heumann [31] determined 8×10^8 kg I as annual mass that enters the atmosphere globally as methyl iodide derived from measurements in Antarctica. The highest value for the global annual transfer of methyl iodide with 1.3×10^9 kg was obtained by Rasmussen *et al*. [32] whose data included regions of relatively high biological activity. These authors stated that the major part of the methyl iodide globally and annually transferred to the atmosphere, 1.0×10^9kg, is transferred at regions of high biological activity that amount to only 10% of the global marine surface. Below we will treat the North Sea as a biologically active region and use Rasmussen's data to estimate the mass of ^{129}I annually transferred from the sea to the atmosphere. Treating the North Sea and the English Channel as areas of high biological activity may justify neglect of the transfer of iodine compounds other than methyl iodide.

3.1 Relative contributions of liquid and gaseous ^{129}I emissions

The answer to the question whether liquid or gaseous releases dominate the ^{129}I concentrations in precipitation in central Europe is of general interest in the near future because the time dependence of these two types of emissions has been quite different (see below).

Investigations into the following four questions may help solve the above puzzle: 1) Are the ^{129}I/^{127}I ratios in the North Sea and in the English Channel sufficient to explain iodine isotopic ratios in the precipitation in central Europe? 2) Is the amount of ^{129}I that is transferred from the sea to the atmosphere with a sufficiently high ^{129}I/^{127}I ratio enough for the precipitation in central Europe and how does this amount compare to the mass of ^{129}I directly released into the atmosphere? 3) Do the ^{129}I concentrations in precipitation in central Europe correlate better with the time dependence of the liquid or that one of the gaseous emissions of the two reprocessing plants? 4) Can the large scatter in monthly ^{129}I concentrations be explained by different source regions of the air masses especially at the days with precipitation during the respective months?

The first question cannot be answered unambiguously. If one took the isotopic ratios determined by Raisbeck *et al*. [12] as late as 1991 and 1993 in the central North Sea and close to southern Norway as representative, the North Sea could not be the dominant source of ^{129}I in precipitation. Consequently, a substantial, if not dominant, contribution from the gaseous releases would be needed to reach an ^{129}I/^{127}I ratio of about 5×10^{-7}. However, if the iodine isotopic ratios in the early 1990s were already as high as determined by Szidat *et al*. in the late 1990s close to Cuxhaven [7], ^{129}I/^{127}I ratios and ^{129}I concentrations in precipitation could be explained with a marine input alone. Because the sea water flow from the English Channel into the North Sea is dominated by currents close to the coast and neither sea water nor seaweed samples close to the Dutch and German coast from the end of the 1980s and begin of the 1990s have been analyzed, an attempt to estimate the ^{129}I/^{127}I ratios in that region should be worthwhile especially because it should constitute a zone of relatively high biological activity also due to large flat tidal areas. An easy attempt to carry out this task is to take the coastal sample from that time period that is closest to that region and scale it using a transport model. This sample is the sample No.11 in [12] close to Gravelines, where 3.1×10^{-7} as ^{129}I/^{127}I ratio was found in 1991. For scaling, the ratio of the isotopic ratios between the respective boxes (Nos. 105 and 109) of the box model from Nielsen [33] as applied by Szidat [28] is taken yielding in an ^{129}I/^{127}I ratio of 1.6×10^{-7} for the northern

Dutch and German coastal area. Other possibilities as to scale up the results from Raisbeck *et al*. [8] for the seaweed samples at Utsira (southern Norway) to that region close to the Dutch and the German coast are considered much more complicated due to the effect of water masses passing regions of very different depths and will not be carried out here. So we estimate ratios higher than those determined by Raisbeck in the central North Sea [12] but lower by about factor of 3 than the ratios needed to explain $^{129}I/^{127}I$ ratios in precipitation in central Europe for the northern Dutch and German coastal regions. For the Belgian and western Dutch coastal region, the experimental result of 3.1×10^{-7} for $^{129}I/^{127}I$ at Gravelines [12] is taken as an upper limit for the begin of the 1990s, which is around a factor of 2 lower than the isotopic ratio needed.

Below we want to use these estimates to determine the sea surface that could give rise to the transfer of an $^{129}I/^{127}I$ ratio of 5×10^{-7} to the atmosphere in the early 1990s. The underlying areas in the English Channel and coastal regions of the North Sea are shown in Fig. 2. As described above, 1.6×10^{-7} is used as $^{129}I/^{127}I$ ratio for area IV of 19 000 km^2 and 3.1×10^{-7} is used for area III which amounts to 18 000 km^2. Based on the measurements of Raisbeck *et al*. [12] we used 2.5×10^{-6} as $^{129}I/^{127}I$ ratio for area I (5000 km^2) and 5×10^{-7} for the 29 000 km^2 of area II. A sea surface of 70 000 km^2 with an isotopic ratio of 5×10^{-7} in the early 1990s affected by liquid emissions from La Hague is the result of our calculation.

Because the marine discharges from La Hague amounted to 73% of the total liquid emissions of the two reprocessing plants from 1988–1992 [8, 18], this area may be scaled up to 96 000 km^2 to include areas of the Irish Sea affected by liquid discharges from Sellafield. Furthermore, an $^{129}I/^{127}I$ ratio of 5×10^{-7} is considered a lower limit for the iodine isotopic ratio in precipitation in the early 1990s in central Europe. For the iodine flux from the sea to the atmosphere, the publication of Rasmussen *et al*. [32] is used as basis. These authors give a flux of $1 \times 10^{+9}$ kg I/a from areas of high biological activity that amount to only 10% of the global sea surface, *i.e*. 3.5×10^7 km^2. Using that flux density of 28.6 kg I/km^2, the affected sea surface of 96 000 km^2 calculated above and an isotopic ratio of 5×10^{-7}, 1.37 kg ^{129}I are estimated as an upper limit for the mass annually transferred from the affected sea area. We would like to emphasize that we treated the whole area in Fig. 2 as well as a region in the Irish Sea as regions of high biological activity. For the precipitation in central Europe about 760 g ^{129}I per year are needed, when an area of 10^6 km^2 and an annual deposition rate of 5 mBq m^{-2} a^{-1} are used as basis. For a more reliable estimate, the iodine transfer in the North Sea and the English Channel itself has to be studied. Nevertheless, about 6.5 kg ^{129}I [9, 10, 18] emitted annually from Sellafield and La Hague to the atmosphere from 1991 to 1996 (without 1993 for which we have no data for Sellafield) can preliminarily be compared to this 1.37 kg. Based on this comparison, it is very likely that the gaseous emissions do contribute substantially to the precipitation in central Europe even when the large uncertainties of the comparison are taken into account. It is emphasized again that a more precise determination of the transfer factor for iodine from the sea to the atmosphere at the location of interest itself is needed to better estimate the relative contributions of liquid and gaseous discharges to the precipitation in central Europe.

To answer the third question about the correlation of the time dependences of gaseous and liquid ^{129}I emissions with the ^{129}I concentrations in precipitation in central Europe since 1988 the respective data are plotted in Fig. 3. In that figure, ^{129}I concentrations in precipitation as well as both types of releases are normalized to their respective values in 1988. The liquid discharges were enhanced by a factor of 6.4 from 1988 to 1996. This increase has been observed, as stated above, in seaweed samples at the coast of south-

Fig. 2. Areas of the English Channel and coastal areas of the North Sea used as basis to estimate the area with an $^{129}I/^{127}I$ ratio of around 5×10^{-7} at the early 1990s. The $^{129}I/^{127}I$ ratios taken for the different zones are: 2.5×10^{-6} for zone I, 5×10^{-7} for II, 3.1×10^{-7} for III, and 1.6×10^{-7} for IV.

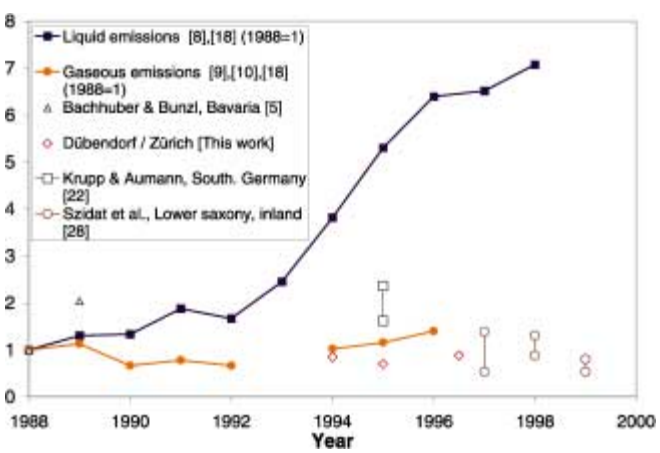

Fig. 3. Liquid and gaseous discharges from La Hague plus Sellafield normalized to their respective values at 1988 and ^{129}I concentrations in precipitation in central Europe also normalized to the concentration in 1988. One scale unit corresponds to 50.5 kg ^{129}I for the liquid emissions and to 6.89 kg ^{129}I for the gaseous emissions, for the ^{129}I concentrations one scale unit is equal to 3.75×10^9 atoms ^{129}I/kg precipitation. Data points connected by a vertical line show the range of the respective data.

ern Norway [8]. In contrast to this the gaseous emissions from Sellafield and La Hague remained approximately constant during that period and exhibited only an increase by a factor of 1.4 from 1988 to 1996 [9, 10, 18]. The ^{129}I concentrations determined in central Europe since 1988 show only a weak, if any, time dependence. Consequently, the ^{129}I concentrations in precipitation are in much better agreement with the time dependence of the gaseous emissions of the two reprocessing plants than with their liquid releases.

The month-to-month variations in ^{129}I concentrations (cf. Table 1) might be related to differences in the source regions and atmospheric transport conditions of the air masses that lead to the sampled precipitation close to Zürich. For instance, large monthly ^{129}I concentrations might be a consequence of many rain events during the months with advection directly from La Hague or from Sellafield and with no or only a few rain events with transport from a different source region which would dilute the measured ^{129}I precipitation concentrations. Additionally for the air masses advected from the La Hague/Sellafield region it is important that no (or little) precipitation occurs before they reach the measurement site. On the other hand, low monthly ^{129}I concentrations can be expected when the air mass advection is not from the La Hague/Sellafield region on rainy days in Zürich, or when the air parcels have lost their ^{129}I atoms due to wet scavenging on their way to central Europe, or when significant dilution occurs from rain events with other source regions.

In order to test the influence of atmospheric transport, three-dimensional assimilated wind fields from the European Center for Medium-Range Weather Forecast (ECMWF) are used to calculate backward trajectories [34] for two high ^{129}I months May 1994 (9405) and May 1997 (9705), and two low ^{129}I months November 1994 (9411) and December 1996 (9612). The wind fields are globally available every 6 hours on a latitude/longitude grid with a horizontal resolution of 1 degree and on 31 vertical levels (therefrom about 14 in the lowest 5 km). Note that assimilated data constitute a "sophisticated combination" of a short-range numerical model forecast and all globally available surface and upper-air observations. A set of 19 trajectories is started between 950 hPa and 400 hPa at Dübendorf every 6 hours during a selected month, and then calculated 72 hours backward in time. Daily precipitation data for Dübendorf was provided by the ANETZ measurement station of the Swiss Meteorological Institute in Zürich, which is situated about 10 km from Dübendorf. The total amount of precipitation for the selected four months are: 234.2 mm in 9405, 54.3 mm in 9705, 43.0 mm in 9411, and 78.5 mm in 9612.

Fig. 4 shows an example for atmospheric transport from the La Hague/Sellafield region to the measurement site on 8 May 1997. Furthermore, two regions around each of the source regions La Hague and Sellafield are marked, which we considered for liquid and gaseous emissions.

The results of the trajectory calculations are summarized in Table 4a and 4b, which are based upon those trajectories that satisfy the following two criteria: The backward trajectory started at Dübendorf hits at least one of the four source regions marked in Fig. 4, and the precipitation in Zürich exceeds 1 mm on the starting day of the trajectory. Table 4a gives the number of days per month where these two criteria are fulfilled. During the high ^{129}I months May 1994 and May 1997, the La Hague source region is more often "connected" to the measurement site than during the low ^{129}I months Nov. 1994 and Dec. 1996. On the other hand, this is not true for Sellafield, for where no significant differences can be discerned. Further information can be gained from Table 4b which answers the question how much of the monthly precipitation can be potentially loaded with ^{129}I. For instance, 22% of the precipitation which was measured in May 1994 in Zürich, was due to condensation in air masses coming from the La Hague marine region. If differences in the source regions and atmospheric transport conditions

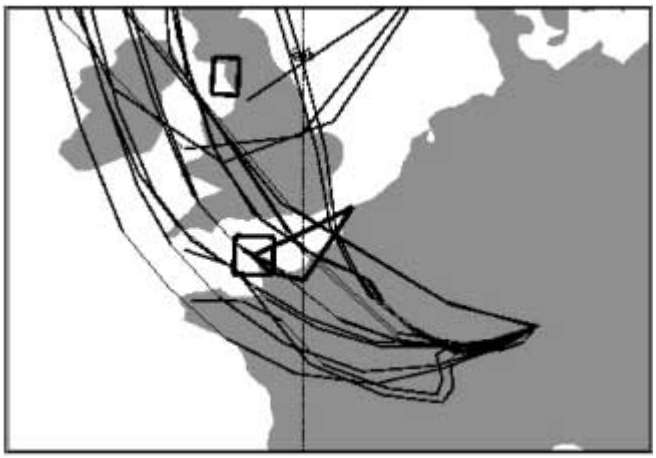

Fig. 4. An illustrative example for atmospheric transport from the La Hague region to Dübendorf. Shown are 19 backward trajectories starting at 18 UTC 8 May 1997 in Dübendorf on different vertical levels and the assumed source regions for ^{129}I in La Hague (atmospheric and marine) and Sellafield (similar boxes for atmospheric and marine). Some of the trajectories travel through the La Hague source regions 1 to 2 days before arriving at Dübendorf.

Table 4a. The number of days which satisfy the following criteria: (a) The backward trajectory started from Dübendorf hits one of the four source regions, and (b) the precipitation in Zürich exceeds 1 mm. Note that the months May 1994 (9405) and May 1997 (9705) show high ^{129}I concentrations, and that the months November 1994 (9411) and December 1996 (9612) low ^{129}I values.

	9405	9411	9612	9705
La Hague marine	6	2	3	4
La Hague atmospheric	6	3	2	3
Sellafield marine	1	2	1	1
Sellafield atmospheric	1	2	1	1

Table 4b. The percentage of monthly precipitation in Zürich which is associated with condensation in air masses coming from one of the four source regions. The analysis is based upon the same trajectories as the ones used in Table 4a.

	9405	9411	9612	9705
La Hague marine	22	27	19	33
La Hague atmospheric	23	33	15	19
Sellafield marine	2	15	7	10
Sellafield atmospheric	2	30	7	10

alone were able to explain the large month-to-month variations, we would expect to see similar variations in Table 4b as for ^{129}I concentrations in Table 1. However, the variability which can be attributed to atmospheric transport is much smaller than what has been observed for ^{129}I concentrations in precipitation, when constancy of the gaseous emissions with time is assumed.

Two possible explanations for this discrepancy relate to the atmospheric transport from the source regions to the measurement site itself, and to the variability of the gaseous release of ^{129}I. These two issues will be briefly discussed. We assumed that the emitted ^{129}I (for instance from La Hague) will be rained out in Zürich if the trajectory "connects" the source with the measurement site. But wet scavenging of an air parcel before its arrival at the measurement site might, in fact, considerably reduce the amount of ^{129}I rained out later in Zürich. The consideration of this effect is, however, very difficult given the coarse temporal resolution (24 hours) of the precipitation measurements over Europe. For the second issue, additional qualitative information can be gained from weekly ^{85}Kr measurements in Freiburg im Breisgau [35], which is located about 120 km from Zürich. High ^{85}Kr concentrations may indicate high gaseous ^{129}I emissions, whereas low ^{85}Kr concentrations point to low gaseous ^{129}I discharges. It must however be emphasized that ^{85}Kr unlike ^{129}I is not washed out by precipitation, and that the distance between Freiburg and Zürich allows only qualitative inferences. In the high ^{129}I months, precipitation associated with transport from La Hague/Sellafield occurs during the weeks with high ^{85}Kr concentrations (for instance, the precipitation event on 22 May 1997 goes along with a weekly ^{85}Kr value of 2.73 mBq/m^3, and the one on 28/29 May 1994 with 1.97 mBq/m^3). On the other hand, lower ^{85}Kr concentrations (mostly below 1.4 mBq/m^3) are typical for the low ^{129}I months.

To summarize, the trajectory-based analysis cannot account for the large month-to-month variations of the ^{129}I of two orders of magnitude, and suggests that they could be due to variable gaseous emissions or due to wet scavenging between the source regions and Zurich. More detailed investigations would be highly desirable, if possible based upon weekly ^{129}I samples and upon the now published monthly data of gaseous halogen emissions [36], that are available on the internet. These new release data for La Hague indicate that the gaseous ^{129}I discharges have been decreased by about a factor of 6 from 1996 to 2000. Unless a similar reduction was achieved at Sellafield, the British reprocessing plant should dominate the gaseous ^{129}I releases in 2000.

A last attempt to distinguish between marine or atmospheric ^{129}I is to look at the seasonal variation in our data. Whereas four of the five highest monthly ^{129}I concentrations were found in spring, Rasmussen *et al*. [32] found a maximum in methyl iodide transfer from the sea to the atmosphere during summer. Consequently, we tend to assume that high ^{129}I concentrations in spring do not reflect an increase in biological activity in the North Sea, but may be more likely due to high gaseous discharges during the respective months as indicated by ^{85}Kr measurements in Freiburg im Breisgau [35] and by monthly ^{85}Kr emission data from La Hague [36].

4. Conclusions

It has been confirmed that ^{129}I concentrations in rain in central Europe have not been increased further within the measurement uncertainties until 1997 compared to the already strongly elevated concentrations analyzed for the late 1980s. Typical ^{129}I atom concentrations in rain in Switzerland in the years 1994 to 1997 are on the order of 10^9 at/kg but exhibit strong variations. The deposition rates determined for Dübendorf in the mid 1990s are a bit lower than but of the same order of magnitude as those determined in Germany for 1995 and 1997/98. The time dependence of the ^{129}I concentrations in precipitation in central Europe that have been analyzed since 1988 is in much better agreement with the gaseous emissions from the reprocessing plants at Sellafield and La Hague than with the liquid releases from these sites. Using a transfer factor for iodine from the sea to the atmosphere, that was not determined in the area of interest itself, the gaseous emissions of the two nuclear fuel reprocessing plants constitute the bigger ^{129}I reservoir compared to the iodine from the liquid emissions that has been transferred into the atmosphere. In order to better estimate these two reservoirs, a determination of this transfer factor is considered necessary in the North Sea and the English Channel itself. The high month-to-month variability of the ^{129}I concentrations in the precipitation samples could not be explained by changes in atmospheric transport alone. Comparison with ^{85}Kr data from Freiburg im Breisgau may indicate some, even short-term, time dependence of gaseous releases from the reprocessing plants. But also a possible effect of *e.g.* wet scavenging of ^{129}I between the emission sources and the sampling site has to be taken into account. The chances to explain the month-to-month scatter in ^{129}I concentrations in precipitation should be higher for weekly sampling because more detailed transport calculations would be feasible, also based upon higher resolution numerical data sets. In addition, a more reliable indicator of atmospheric emissions than ^{85}Kr measured with weekly resolution at some distance from the sampling site is needed to address the question of the relative contributions of marine and atmospheric ^{129}I emissions to the precipitation in central Europe more exactly. Due to the very different time dependence of liquid and gaseous releases of ^{129}I from the two major nuclear reprocessing plants, the development of ^{129}I concentrations in precipitation in future depends on whether the gaseous or the liquid discharges are the dominant source.

Acknowledgment. The preparation of some of the samples by S. Bollhalder-Lück (EAWAG) is gratefully acknowledged. Discussions with R. Michel and T. Ernst (ZSR, Universität Hannover) are greatly appreciated. In refereeing this manuscript, Peter H. Santschi and Kathy Schwehr made helpful comments and improved the English style. This work has been supported in part by the German National Science Foundation (DFG), Bonn and by the Swiss National Science Foundation (SNF), Bern. MS has been supported through the EU project STACCATO under contract BBW 99.0582-2 resp. EVK2-CT-1999-00050.

References

1. Snyder, G., Fehn, U.: ^{129}I in volcanic fluids: Testing for the presence of marine sediments in the Central American volcanic arc. Nucl. Instrum. Methods Phys. Res. B **172**, 568 (2000).

2. Schmidt, A., Schnabel, Ch., Handl, J., Jakob, D., Michel, R., Synal, H.-A., Lopez, J. M., Wagner, M. J. M., Suter, M.: On the analysis of I-129 and I-127 in environmental materials by accelerator mass spectrometry. Sci. Total Environ. **223**, 131 (1998).
3. Wagner, M. J. M., Dittrich-Hannen, B., Synal, H.-A., Suter, M., Schotterer, U.: Increase of ^{129}I in the environment. Nucl. Instrum. Methods Phys. Res. B **113**, 490 (1996).
4. Wagner, M. J. M.: *Mittelschwere Radionuklide: Neue Nachweismethoden und Anwendungen von Nickel-59, Zinn-126 und Iod-129*. Ph.D. Thesis ETH No. 11 294, 1995 Zürich (in German).
5. Bachhuber, H., Bunzl, K.: Background levels of atmospheric deposition to ground and temporal variations of ^{129}I, ^{127}I, ^{137}Cs and ^{7}Be in a rural area of Germany. J. Environ. Radioactivity **16**, 77 (1992).
6. Szidat, S., Schmidt, A., Handl, J., Jakob, D., Michel, R., Synal, H.-A., Schnabel, Ch., Suter, M., Lopez-Gutierrez, J. M.: RNAA and AMS of Iodine-129 in environmental materials – comparison of analytical methods and quality assurance. Kerntechnik **65**, 160 (2000).
7. Szidat, S., Schmidt, A., Handl, J., Jakob, D., Botsch, W., Michel, R., Synal, H.-A., Schnabel C., Suter, M., Lopez-Gutierrez, J. M., Städe, W.: Iodine-129: Sample preparation, quality control and analyses of pre-nuclear materials and of natural waters from Lower Saxony, Germany. Nucl. Instrum. Methods Phys. Res. B **172**, 699 (2000).
8. Raisbeck, G. M., Yiou, F.: ^{129}I in the oceans: origins and applications. Sci. Total Environment **237**/**238**, 31 (1999).
9. Gray, J., Jones, S. R., Smith, A. D.: Discharges to the environment from the Sellafield Site 1951–1992. J. Radiol. Prot. **15**, 99 (1995).
10. BNFL: Annual Report on Discharges and Monitoring of the Environment, 1998, British Nuclear Fuel, Risley (1999).
11. Fabryka-Martin, J.: Natural ^{129}I as a ground-water tracer. M.Sc. Thesis, Univ. of Arizona (1984).
12. Raisbeck, G. M., Yiou, F., Zhou, Z. Q., Kilius, L. R.: ^{129}I from nuclear fuel reprocessing facilities at Sellafield (U.K.) and La Hague (France); potential as an oceanographic tracer. J. Marine Systems **6**, 561 (1995).
13. Eisenbud, M., Gesell, T.: *Environmental Radioactivity*. 4th ed., Academic Press, San Diego (1997) p. 556.
14. Carter, M. W., Moghissi, A. A.: Three decades of nuclear testing. Health Phys. **33**, 55 (1977).
15. UNSCEAR report, United Nations Scientific Committee on the Effects of Atomic Radiation reports to the General Assembly of the United Nations, New York (1982).
16. Paul, M., Fink, D., Hollos, G., Kaufman SA, Kutschera, W., Magaritz, M.: Measurement of ^{129}I concentrations in the environment after the Chernobyl reactor accident. Nucl. Instrum. Methods Phys. Res. B **29**, 341 (1987).
17. The release of radioactive material from Hanford: 1944–1972: the Hanford Health Information Network (*http://www.doh.wa.gov/hanford/publications/history/release.html*).
18. Inventaire des rejets radioactifs des installations nucléaires: Historique des rejets, Rapport Finale Détaillé Vol. I, Groupe Radioécologie Nord-Cotentin GT1, c/o Institut de Protection et de Sûreté Nucléaire, Fontenay-aux-Roses, 1999 (in French).
19. Schink, D. R., Santschi, P. H., Corapcioglu, O., Sharma, P., Fehn, U.: ^{129}I in Gulf of Mexico waters. Earth Planetary Sci. Lett. **135**, 131 (1995).
20. Whitehead, D. C.: The distribution and transformations of iodine in the environment. Environment International **10**, 321 (1984).
21. Dean, G. A.: The iodine content of some New Zealand drinking waters with a note on the contribution from sea spray to the iodine in rain. New Zealand J. Sci. **6**, 208 (1963).
22. Krupp, G., Aumann, D. C.: Iodine-129 in rainfall over Germany. J. Environmental Radioactivity **46**, 287 (1999).
23. Lopez-Gutierrez, J. M., Synal, H.-A., Suter, M., Schnabel, Ch., Garcia-Leon, M., Accelerator mass spectrometry as a powerful tool for the determination of ^{129}I in rainwater. Appl. Radiat. Isot. **53**, 81 (2000).
24. Lopez-Gutierrez, J. M., Garcia-Leon, M., Garcia-Tenorio, R., Schnabel, Ch., Suter, M., Synal, H.-A., Szidat, S.: ^{129}I/^{127}I ratios and ^{129}I concentrations in a recent sea-sediment core and in rainwater from Seville (Spain) by AMS. Nucl. Instrum. Methods Phys. Res. B **172**, 574 (2000).
25. Fuge, R., Johnson, C. C., The geochemistry of iodine – a review. Environ. Geochem. Health **8**, 31 (1986).
26. Moran, J. E., Oktay, S. D., Santschi, P. H., Schink, D. R.: Atmospheric dispersal of ^{129}I from European nuclear fuel reprocessing facilities. Environ. Sci. Technol. **33**, 2536 (1999).
27. Yiou, F., Raisbeck, G. M., Zhou, Z. Q., Kilius, L. R.: ^{129}I from nuclear reprocessing: potential as an oceanographic tracer. Nucl. Instrum. Methods Phys. Res. B **92**, 436 (1994).
28. Szidat, S.: Iod-129: Probenvorbereitung, Qualitätssicherung und Analyse von Umweltmaterialien. Ph. D. thesis, University of Hannover (2000) (in German).
29. Rucklidge, J., Kilius, L., Fuge, R.: ^{129}I in moss down-wind from the Sellafield nuclear fuel reprocessing plant. Nucl. Instrum. Methods Phys. Res. B **92**, 417 (1994).
30. Moran, J. E., Oktay, S., Santschi, P. H., Schink, D. R.: Surface ^{129}iodine/^{127}iodine ratios: marine *vs*. terrestrial, AIP Conference Proceedings. In: *Applications of Accelerators in Research and Industry*. (Duggan, J. L., Morgan, I. L. eds.) New York (1997) Vol. 392, pp. 807–810.
31. Reifenhäuser, W., Heumann, K. G.: Determinations of methyl iodide in the Antarctic atmosphere and the south Polar Sea. Atmos. Environ. **26A**, 2905 (1992).
32. Rasmussen, R. A., Khalil, M. A., K., Gunawardena, R., Hoyt, S. T.: Atmospheric methyl iodide (CH_3I). J. Geophys. Res. **87**, 3086 (1982).
33. Ali, S. M., Beaumont, H. M., Dutton, L. M. C., Handy, B. J., Hosty, M., Parsons, A. F., Nielsen S. P., Sivintsev, Y., Lystsov, V., Yefimov, E. I., Sazykina, T., Zheleznyak, M., Maderich, V., Margvelashvili, N.: Evolution of the radiological situation around the nuclear reactors with spent fuel which have been scuttled in the Kara Sea. European Commission, Report EUR 17634 EN (1997).
34. Wernli, H., Davies, H. C.: A Lagrangian-based analysis of extratropical cyclones. I: The method and some applications. Quart. J. Roy. Meteor. Soc. **123**, 467 (1997).
35. Sartorius, H.: Bundesamt für Strahlenschutz Jahresbericht 1998. ISSN 0940-7650, p. 67.
36. Cogema, La Hague: *http://www.cogemalahague.com*.